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Subject: Technical Letter 24
Removal of Water Supply Contaminants -- Selenium

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This is the tenth in a series of Technical Letters dealing with state of the art methods for removal of contaminants from water supplies so that the supply will be in compliance with state and federal drinking water standards.

Contaminant

This Technical Letter is concerned with selenium (Se) as a contaminant of drinking water. In 1976 there were no water supplies in use in the state of Illinois which exceeded the drinking water standard of 0.01 milligram per liter (mg/l) according to the Illinois Environmental Protection Agency.

Prevalence and Uses

Selenium is considered to be an essential trace element for good health. Selenium has been shown to be involved in several metabolic pathways. Selenium is also highly toxic. The difference between safe and toxic levels of selenium is only about a factor of two.

Selenium is found widely distributed in nature at low levels. Some soils contain relatively high levels of selenium; however, these are mainly found in the western United States. Selenium is associated with sulfide ores and is generally obtained as a by-product of the refining of sulfide ores, mainly copper. Selenium is found in groundwater supplies as a result of leaching of geological deposits containing selenium or from contamination by industrial usage.

Selenium is sensitive to light which has made it useful in photoelectric cells. Selenium is used in the electronics industry for rectifiers, photo cells, solar batteries, television cameras, and xerography. It is used as a decolorizer for glass and ceramics and as the red pigment in ruby glass, ceramics, enamels, and permanent labels on bottles. Selenium and its compounds are used as vulcanizing agents for rubber, to etch steel, as an oxidizing agent in the preparation of niacin and cortisone, as an anti-oxidant in lubricating and other oils, as a toning agent for photographic prints, to increase the machinability of stainless

steel, as a brightener for copper plating, as a solvent for synthetic resins, and as a paint, varnish, and glue remover. It is also used in control of dandruff, as an insecticide and fungicide, and in insect repellents. It is used in fertilizer or as a feed supplement in areas where soil is deficient in selenium.

Health Effects

Selenium is considered to be a necessary trace element, and is required at very low levels for good health. Deficiencies are very rare, as a result of adequate dietary levels of selenium, particularly in meats and grains.

Selenium exhibits a narrow range between acceptable intake and toxic intake.. Ingestion of as little as 10 mg/g as food or 10 mg/l as water can result in acute toxic effects. Symptoms of selenium poisoning are discolored and decayed teeth, yellow skin color, skin eruptions, chronic arthritis, atrophic brittle nails, edema and gastrointestinal disorders, and, in some cases, lassitude and partial or total loss of hair and nails. The toxicity of selenium varies depending on whether it is in the selenite or selenate form. In studies with rats, selenite appears to be more toxic than selenate.

Concern about selenium in water is based on its chronic effects. Selenium is included in a list of carcinogenic agents by the Food and Drug Administration. Studies with rats have shown that ingestion of low levels of selenium can cause tumors in some rats. Studies with shorter-lived rats did not produce cancer. Additional studies have shown that selenium inhibits tumor formation when ingested in combination with other known chemical carcinogens.

Some researchers have suggested that lower dietary selenium levels may be a factor in the increased level of breast cancer in Western women compared with Asian women.

Selenium has also been implicated as playing a role in reducing the incidence of heart disease. The heart disease rate has been found to be lower in states with high selenium levels in the soil. The actual role of selenium in heart disease is unclear at the present time. The exact health effects, whether harmful or beneficial, are not clearly defined for selenium. The drinking water standard is based on the reported adverse health effects.

Maximum Levels

The maximum allowable level of selenium for drinking water is 0.01 mg/l.

Removal

Selenium will exist in waters as an anionic species. It will be as the +4, selenite (Se O_3^{-2}) or the +6, selenate (Se O_4^{-2}) forms. Both species form soluble salts with sodium, potassium, and calcium. Selenite can be oxidized to selenate by permanganate or chlorine while selenate is not easily reduced to selenite.

A. Coagulation with Sedimentation

Coagulation involves the addition of aluminum or iron salts with lime or carbonate to control the pH at 9 to 11. This results in the formation of gelatinous precipitates of hydrated oxides. The precipitates will occlude other species present in solution and carry them down. The efficiency of this method depends on the solubility of the material to be removed. Neither selenite nor selenate forms insoluble compounds at high pH. Their iron and aluminum salts are slightly soluble, making this method somewhat inefficient for selenium removal. The selenite form is somewhat less soluble than selenate so slightly better removal efficiencies are achieved. The Federal Environmental Protection Agency reports that 60 to 90 percent removal of selenium IV is achieved at a maximum concentration of 0.1 mg/l whereas only 0 to 30 percent removal for selenium VI is observed at a maximum concentration of 0.015 mg/l. The actual efficiencies will depend on the nature of the water being treated. The method is essentially useful only for selenium removal if all the selenium is present as selenite. Reduction of selenate to selenite requires use of concentrated hydrochloric acid or other strong reducing agents. It is unlikely that reduction of selenate to selenite prior to coagulation will be a very easily applied process. It is possible that ferrous iron might work in reducing selenate to selenite although this has not been investigated.

B. Lime Soda Softening

Lime soda softening involves the reduction of calcium and magnesium hardness by precipitation of calcium carbonate and magnesium hydroxide. The lime which is added raises the pH to between 10 and 11; soda is added to provide sufficient carbonate ion. Other species present which form insoluble oxides or insoluble carbonates at the high pH are also removed along with the calcium and magnesium. This process is not very efficient in removing selenium. Both selenate and selenite are soluble at the high pH. Also their calcium salts are soluble. The selenite is less soluble than selenate so that the efficiency of removal is somewhat better for selenite.

The Federal EPA reports efficiencies of 60 to 90 percent for removal of selenite with a maximum concentration range of 0.025 to 0.1 mg/l. The efficiency of removal of selenate is only 0 to 30 percent at a maximum concentration of 0.015 mg/l making the method relatively useless for removal of selenium when present as selenate. Removal efficiencies are strongly dependent on the nature of the water being treated. The potential for reduction of selenate to selenite to improve removal efficiency for selenate does not appear to be a promising approach.

C. Reduction and Precipitation

Improved removal efficiencies would be anticipated if prior treatment with sulfur dioxide (SO_2) was carried out before coagulation with aluminum or iron or lime soda softening. The addition of SO_2 will result in the reduction of selenite to elemental colloidal selenium. This should be effectively carried down during the coagulation or softening process. Unfortunately selenate is not affected by this process. Additional treatment would be necessary to reduce selenate to selenite prior to SO_2 reduction or else a stronger reductant would be necessary to reduce both selenate and selenite to elemental selenium. No readily convenient method for accomplishing this is available.

D. Ion Exchange

Ion exchange will be effective in removing both selenite and selenate from water. The process involves the exchange of the ions to be removed with the ions from the ion exchanger. Since selenium will exist as negatively charged species, an anion exchange column can be used. The selenium in solution will be replaced by chloride from the anion exchanger resin. Since a resin specific for selenium is not available, other anions in solution such as carbonate, sulfate, etc., will also be removed. This will not affect the removal of selenium except to decrease the resin capacity for selenium and to require more frequent resin regeneration. Some adjustment of pH may be necessary to insure that both selenite and selenate are present as the dissociated anions.

If the amount of chloride introduced into the treated water should become objectionable, complete demineralization of the water using a combination of anion and cation exchange beds will be necessary. This involves the replacement of cations with hydrogen and the replacement of anions with hydroxide. The hydrogen and hydroxide ions will react to produce water. This is a much more costly procedure. Treatment of the finished water will be required to prevent corrosion of the distribution system.

It may not be necessary to treat all the water. Treated water may be blended with untreated water to produce a finished water with an allowable selenium level. The ratio of treated to untreated water depends on the level of selenium in the raw water. Because resins that can specifically remove selenium are not available, ion exchange treatment to remove specific contaminants will be costly.

E. Reverse Osmosis

Reverse osmosis involves the removal of soluble minerals by passage of water through a semipermeable membrane. To get water to pass through the membrane it is necessary to apply pressure to the water containing the minerals to overcome the natural direction of flow which would be

for pure water to diffuse into the mineral-containing water. The amount of pressure necessary is dependent on the mineral content of the raw water.

Although reverse osmosis can be used to reduce the selenium level, its application is impractical and costly unless it is already in use for the treatment of brackish water. The most significant cost is plant construction. For a 1000 m³/day plant (183 gpm), construction costs will be about \$250,000 based on 1976 costs. This cost does not include costs for any interest during construction, site and site improvement, discharge facilities, storage and delivery facilities, or special treatment. Operating costs are about \$18,000 for a plant of that capacity.

F. Electrodialysis

Electrodialysis involves the removal of salts by means of ion selective membranes and a d.c. current to assist transport of the ions across the membrane. There is depletion of ions on one side of the membrane if current is passed for any length of time, while there is concentration on the other side of the membrane. Any level of desalting can be achieved by increasing the residence time or increasing the current density.

For efficient operation good water pretreatment is required. This should include coagulation of colloidal particles, oxidation of iron and soluble organics, carbon filtration, and finally acidification.

Although this process can be used for the reduction of selenium levels, its application is impractical and costly even if other contaminants are to be removed unless the equipment is already in use or planned for use to reduce brackish water to an acceptable salt level. The cost for electrodialysis depends on the level of contaminant to be reduced. In general it will be more costly than reverse osmosis. The pH of the effluent may require adjustment to protect the distribution system.

G. Distillation

Distillation involves the volatilization of water to separate it from all dissolved or suspended materials which are not volatilized. Normally the water is heated under pressure to improve the thermal efficiency of the method by recovering some of the heat. This process produces water of very low dissolved solids. Since the distilled water is corrosive to the distribution system, it is necessary to increase the hardness. This can normally be accomplished by appropriate blending of the finished water and the raw water.

Some pretreatment of the feedwater may be necessary to remove suspended solids and calcium and magnesium to prevent scaling.

Distillation is a relatively expensive and impractical solution for the removal of specific contaminants from water. The process involves the removal of a large volume of water from a small amount of dissolved material. This results in an unfavorable energy requirement since it is essentially independent of the contaminant level and only dependent on the amount of water to be treated. The major cost is plant construction which will be about \$1.2 million for a 1000 m³/day plant (183 gpm). The operating costs for energy are also high, since there is only partial heat recovery in this process.

General Comments

All of the removal techniques discussed above require pilot-scale testing for a specific application to determine their efficiency. Pilot-scale studies are also needed to determine what, if any, pretreatment is necessary to insure good operating efficiency. All of the processes which effectively demineralize the water require some adjustment of pH and/or hardness and alkalinity to prevent corrosion of the distribution system.

Technical Letters are issued as part of the Water Survey's continuing service to citizens of Illinois. Should you need further clarification, please let us know.

Very truly yours,

A handwritten signature in cursive script that reads "Francis Amore".

Dr. Francis Amore
Associate Professional Scientist

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